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[CONTRIBUTION FROM THE FATTY ACID PRODUCERS' COUNCIL OF THE ASSOCIATION OF AMERICAN SOAP AND GLYCERINE PRODUCERS, INC., AND THE EASTERN REGIONAL RESEARCH LABORATORY¹]

Phosphorus Derivatives of Fatty Acids. V.² Vinyl α -Diethylphosphonates

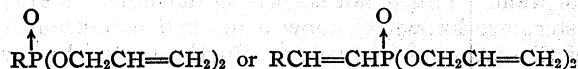
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Vinyl α -bromo esters have been prepared in 30–60% yield from vinyl acetate and the appropriate C₂ to C₁₈ straight chain α -bromocarboxylic acid (equation 1). By heating the vinyl α -bromo esters with triethyl phosphite, the corresponding vinyl α -diethylphosphonates were prepared in 35–75% yield (equation 2). The vinyl α -phosphonates are colorless, odorless liquids which are insoluble in water and soluble in organic solvents. Under prolonged heating with benzoyl peroxide, they form polymers with a low degree of polymerization.

The first three papers in this series,^{4–6} described the preparation and properties of dialkyl acylphosphonates, dialkyl acyloxyethyl phosphonates and trialkyl α -phosphonates, respectively. The present investigation deals with the synthesis and properties of some new vinyl esters of α -diethylphosphonocarboxylic acids.

The literature describes numerous examples of unsaturated esters of phosphonic acids.^{7–10} These compounds have the general formulas



In contrast to alkenyl phosphonates, the literature reports relatively few examples of alkenyl phosphonocarboxylates. The examples appear to be limited to the vinyl (I) and allyl (II) phosphonoacetates.^{11–13} In these compounds, the alkenyl group of the ester is attached to carbon and not to phosphorus as in the previous types.

(1) Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

(2) Presented at the Fall Meeting of the American Chemical Society, Chicago, Ill., September 7–12, 1958. Paper IV in this series, *Ind. Eng. Chem.*, data series (1958).

(3) Fellow of the Fatty Acid Producers' Council of the Association of American Soap and Glycerine Producers, Inc.

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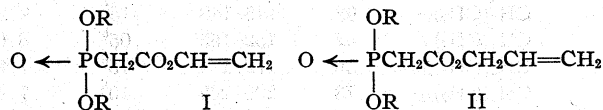
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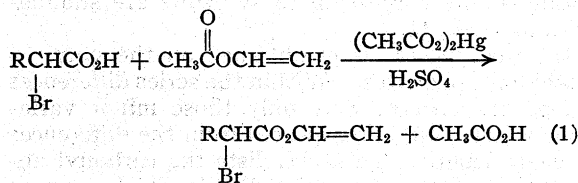
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Apparently there are no reports on the systematic preparation and study of the physical and chemical properties of the vinyl (α -diethylphosphono)carboxylate esters, a previously unreported series of polymerizable esters.

This paper describes the preparation and properties of the vinyl esters of bromoacetic, α -bromocaproic, -pelargonic, -capric, lauric, -myristic, -palmitic and -stearic acids. These compounds, most of which have not been described previously, were prepared from the appropriate α -bromocarboxylic acid and vinyl acetate by acidolysis in the presence of mercuric sulfate.

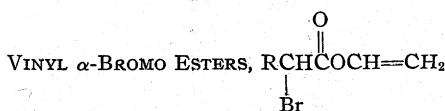


R = H, C₄H₉, C₇H₁₅, C₈H₁₇, C₁₀H₂₁, C₁₂H₂₅, C₁₄H₂₉, C₁₆H₃₃

The properties, yields obtained and analyses of the vinyl α -bromo esters are summarized in Table I. These esters are colorless, odorless (except for the acetate which is strongly lachrymatory), high-boiling liquids insoluble in water and soluble in organic solvents.

By heating the vinyl α -bromo esters with triethyl phosphite in a Michaelis-Arbuzov reaction, the corresponding vinyl α -diethylphosphonates were prepared.

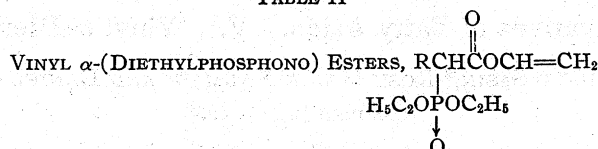
TABLE I



R	Yield, %	B.p.		Bromine, %		n_D^{20}	d_4^{20}	Molecular refraction	
		°C.	Mm.	Calcd.	Found			Calcd.	Found
H-	30	50-51	9.0 ^a	48.4	47.9	1.4692	1.5414	29.88	29.89
CH ₃ (CH ₂) ₃ -	43	84-86	2.8 ^a	20.5	20.2	1.4588	1.2360	48.46	48.88
CH ₃ (CH ₂) ₆ -	30	66-67	0.15 ^a	30.3	30.0	1.4608	1.1566	62.39	62.46
CH ₃ (CH ₂) ₇ -	33	92-94	.20 ^b	28.8	28.4	1.4612	1.1298	67.03	67.30
CH ₃ (CH ₂) ₉ -	46	116-117	.20 ^b	26.2	26.3	1.4617	1.0933	76.32	76.71
CH ₃ (CH ₂) ₁₁ -	58	137-139	.25 ^b	24.0	23.8	1.4627	1.0699	85.61	85.76
CH ₃ (CH ₂) ₁₃ -	30	165-167	.15 ^b	22.1	22.3	1.4633	1.0554	94.89	94.36
CH ₃ (CH ₂) ₁₅ -	33	190-192	.10 ^b	20.5	20.2	1.4641	1.0304	104.2	104.2

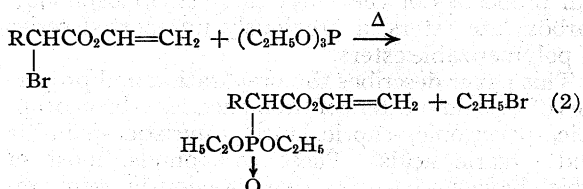
^a Distilled through a heated, jacketed Vigreux column, 60 cm. long. ^b Distilled through a short Claisen head filled with glass tubing.

TABLE II



R	Yield, %	B.p.		Phosphorus, %		n_D^{20}	d_4^{20}	Molecular refraction	
		°C.	Mm.	Calcd.	Found			Calcd.	Found
H- ^{11,12}	41	98-100	0.25 ^a	13.9	14.2	1.4348	1.1245	51.55	51.54
CH ₃ (CH ₂) ₃ -	38	158-159	7.8 ^a	11.1	11.2	1.4370	1.0436	70.13	69.86
CH ₃ (CH ₂) ₆ -	35	148-149	0.01 ^a	9.6	9.2	1.4422	1.0082	84.06	84.14
CH ₃ (CH ₂) ₇ -	62	146-148	.15 ^b	9.2	8.8	1.4426	0.9990	88.71	88.62
CH ₃ (CH ₂) ₉ -	47	152-153	.05 ^b	8.6	8.7	1.4443	.9836	97.99	97.94
CH ₃ (CH ₂) ₁₁ -	39	172-174	.15 ^b	7.9	8.0	1.4459	.9736	107.3	106.9
CH ₃ (CH ₂) ₁₃ -	73	200-202	.10 ^b	7.4	7.6	1.4476	.9659	116.6	115.9
CH ₃ (CH ₂) ₁₅ -	41	165	.002 ^c	6.9	7.3	1.4492	.9596	125.8	124.9

^a Distilled through a heated, jacketed Vigreux column, 60 cm. long. ^b Distilled through a short Claisen head filled with glass tubing. ^c Molecularly distilled.



The vinyl α -diethylphosphonates are colorless, odorless, high-boiling liquids insoluble in water and soluble in organic solvents. The properties, yields obtained and analyses of these esters are summarized in Table II.

Infrared spectra were obtained on the vinyl α -diethylphosphonates. Within the series differences among the spectra were only those minor variations which would be expected from the differences in chain length. Table III lists the carbonyl absorption and the absorption bands which may be associated with the phosphorus-containing portion of the molecule. For comparison, the absorption bands of the trialkyl α -phosphonates are also listed in Table III. The band assignments are taken from Bellamy.¹⁴ The 785-793 cm.⁻¹ bands are also tentatively assigned to P-O-C vibration in accordance with the suggestion of Meyrick and Thompson.¹⁵ As can be seen from Table III, the absorption bands for the trialkyl α -phosphonates

are practically identical with those in the vinyl α -diethylphosphonates except for the carbonyl absorption. This is not surprising inasmuch as vinyl esters are known to show a marked enhancement of the carbonyl frequency. Furthermore, the corresponding band intensities in the two series are essentially identical.

TABLE III
ASSIGNMENT OF ABSORPTION BANDS, CM.⁻¹

	Vinyl α -diethylphosphonates	Trialkyl α -phosphonates
P-O-C	785-793	785-793
P-O (pentavalent phosphorus)	960-970	964-967
P-O-C (aliphatic)	1030-1035	1027-1032
P-O-Ethyl	1150-1165	1156-1168
P→O	1257-1267	1256-1265
C=O	1745-1760	1735-1740

On prolonged heating with 0.2% benzoyl peroxide, the vinyl α -diethylphosphono esters formed very thick viscous oils. In the one case studied, polyvinyl α -(diethylphosphono)-myristate, the weight average molecular weight was found to be only 83,000.

Experimental

All the reactions and distillations described were conducted in an atmosphere of nitrogen.

Starting Materials.—Bromoacetic and α -bromohexanoic acids were commercial products and were used as received. The α -bromomyristic, α -bromopalmitic and α -bromostearic

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(15) C. I. Meyrick and H. W. Thompson, *J. Chem. Soc.*, 225 (1950).

acids were prepared from the appropriate pure fatty acid and bromine in the conventional manner.¹⁶ The melting points of the α -bromo acids were 41–42°, 49–50° and 56–57°, respectively. The remaining α -bromo acids were commercial products which were fractionally distilled before use: α -bromopelargonic acid, b.p. 138° at 0.8 mm.; α -bromocapric acid, b.p. 153–154 at 0.3 mm.; and α -bromolauric acid, b.p. 160–162° at 0.8 mm. Vinyl acetate, b.p. 72–74°, and triethyl phosphite, b.p. 151–155°, were obtained from the commercial grades by fractional distillation.

Vinyl α -Bromoesters.—The procedure of Toussaint and MacDowell¹⁷ was modified slightly. After the vinyl acetate (1.25 moles), α -bromo acid (0.25 mole), mercuric acetate (1.6 g.) and sulfuric acid (0.15 ml.) were heated, the reaction mixture was cooled, dissolved in 150 ml. of ether and washed with water until the washings were neutral to litmus. The ether solution was dried over anhydrous sodium sulfate, the ether was removed by distillation and the product was distilled under diminished pressure. The results are summarized in Table I.

Vinyl α -diethylphosphonates were prepared by heating the vinyl α -bromo esters with a 100% molar excess of triethyl phosphite at 160–190° in an atmosphere of nitrogen. The ethyl bromide was swept out and collected in a Dry Ice trap. The reaction was stopped when the weight of ethyl bromide became constant (usually 4–5 hr.). Generally, 90

to 95% of the calculated amount of ethyl bromide was obtained. The entire reaction mixture was then fractionally distilled to obtain the pure vinyl α -diethylphosphonate. The results are summarized in Table II.

Infrared Studies.—Infrared absorption spectra were obtained with a Beckman IR-3 spectrophotometer, using sodium chloride prisms. A spacer approximately 0.02 mm. thick was used between two sodium chloride windows for the samples.

Polymerization.—A typical long chain vinyl phosphonate, namely, vinyl α -(diethylphosphono)-myristate (5 g.), was heated at 80° with 0.2% benzoyl peroxide for 48 hours. The mixture then was dissolved in 30 ml. of benzene and the polymer was precipitated with 800 ml. of methanol. The methanol solution was decanted and the polymer again was dissolved and precipitated. After the methanol was decanted, the polymer was dried in a vacuum desiccator. It was a thick, very viscous oil. The polymer had a weight average molecular weight of 83,000 by the light scattering method.

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